

## NEW INDUSTRIAL USES OF CORN

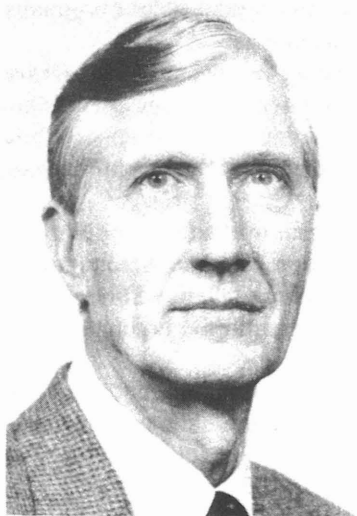
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### Introduction

Although development of new or expanded industrial (non-food) markets for corn has been of concern for several decades, perhaps interest has never been more intense than in recent years. This interest has been fueled by corn production in excess of existing markets that has resulted in ending stocks (surplus) of more than 4 billion bushels (bil. bu.) for each of the last 3 years. Carryover from the 1985 crop of 4,039 bil. bu. plus 1986 production of 8,253 bil. bu. provided a corn supply of nearly 12.3 bil. bu. for 1986. Since the domestic plus export market for corn in 1986 was 6.6 bil. bu., a surplus of nearly 5.7 bil. bu. resulted. Even though 1987 corn production was about 12% less than in 1986, still, ending stocks in excess of 4 bil. bu. will be carried into the 1988 crop year.

Domestic markets for corn increased from about 4.8 to 5.5 bil. bu. during 1983-1986. Domestic processors of corn accounted for most of this increase, and projections are that these processors will continue to use more of the yearly crop. In 1987 we will process about as much corn as we export, an amount above 1.1 bil. bu. Corn processors will buy and process more of the crop as market opportunities expand. Certainly, in-



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creased domestic processing benefits not only American farmers but other sectors of our population as well.

Since starch makes up nearly three-fourths of the corn grain's composition, this component is receiving considerable attention as a raw material from which a variety of low-molecular weight chemicals can be produced that are now obtained from petroleum. Also, research has intensified on starch as a high-molecular-weight polymer to replace certain petroleum-derived polymers and imported gums.

### **Chemicals from Starch**

Although starch can be treated at high temperatures to yield synthesis gas (carbon monoxide and hydrogen), which can be further processed to a number of useful chemicals, it seems unlikely that starches recovered from the processing of cereal grains will be considered to any great extent for such purposes. Rather, the most likely consideration for chemicals from starch will derive from the glucose formed on depolymerization of the polymer.

Such depolymerizations are easily effected. In fact, essentially complete conversion of starch to D-glucose can be realized by successive treatments of a starch slurry with a bacterial alpha-amylase and an amyloglucosidase. Acid hydrolysis can be used in place of the alpha-amylase to liquefy the starch, but overall yields of D-glucose are about 5% lower than with the all-enzyme system.

Glucose can be converted to a variety of alcohols, cyclic and acyclic polyols, aldehydes, ketones, acids (both mono and dibasic), esters, and ethers. Some of these are used industrially now, and others could increase in importance if the price for petroleum and petroleum products continues to rise.

Concern over future supplies of petroleum have revived interest in the production of ethanol from starch to extend our fuel supply. Ethanol is produced in the United States by two major procedures, fermentation and chemical synthesis. Practically all synthetic ethanol is now produced from ethylene.

In 1987 approximately 325 million bushels of corn were used to produce the 800 million gallons of fermentation alcohol in the United States for blending with gasoline. It is projected that production will reach 1 billion gallons in 1990.

Acetic-acid now produced mostly from petroleum-derived ethylene and in small amount from fermentation of sugars has been undergoing evalua-

tion, after conversion to calcium magnesium acetate (CMA), as a deicer salt for highways. In 1982 the Federal Highway Administration initiated a program for complete evaluation of CMA as an alternative deicer to the corrosive sodium chloride-calcium chloride salt now used. Reports from studies conducted under this program and from various other projects and researchers suggest CMA is considerably less corrosive than the salt currently used and would have little deleterious effect on plants or animals. One company marketed the deicer in the 86-87 winter. Although CMA could be derived from synthetic acetic acid or from biomass other than corn, corn growers remain hopeful that a sizeable new market for corn will result from widespread use of CMA.

Several commercially important chemicals can be derived from glucose by fermentation or through chemical conversion, or through combinations of both processes. Tong identified several  $C_3$  and  $C_4$  industrial chemicals that can be produced from sugar via fermentation. These include isopropanol, acetone, n-butanol, 2,3-butylene glycol, glycerol, and fumaric acid. He listed total U.S. production of these chemicals for 1976, and noted that only for acetone (5%), n-butanol (10%) and fumaric acid (15%) was any of the production accounted for by fermentation. A large volume  $C_4$  chemical, butadiene, can be derived from either ethanol or butylene glycol by further chemical treatment. Similarly, methyl ethyl ketone and maleic anhydride can be derived via dehydration from butylene glycol and fumaric acid, respectively.

For increased production of these chemicals via fermentation, Tong suggests five critical areas where improvements in fermentation-related technology are needed: (1) Development of thermophilic organisms capable of producing at temperatures above  $35^{\circ}\text{C}$ , (2) increased conversion efficiencies and/or improved selectivity of products, (3) development of mutant microbial strains that can produce at high rates at high carbohydrate concentrations, (4) development of continuous fermentation processes, and (5) development of byproduct recovery processes for spent fermentation broths. Recent literature and pronouncements by several industrial firms affirm that these areas are receiving attention.

Conversion of starch to chemicals that retain much of the oxygen would be of particular interest. Polyhydroxy compounds, several of which are used in significant quantities, are derivable from glucose. Ethylene glycol ( $4.7 \times 10^9$  pounds), propylene glycol ( $610 \times 10^6$  pounds), and glycerol ( $150 \times 10^6$ , synthetic only) are three such polyols produced in substantial quantities in this country that can be produced from glucose via selected chemical reactions. Ethylene glycol also can be produced in good yield

from dialdehyde starch. This process could become an important route to these polyols if dialdehyde starch is made available at a cost substantially lower than at present.

Sorbitol is probably the most widely used polyol made from starch or glucose. Nearly 180 million pounds was produced in the U.S. in 1979. It is used extensively for making surfactants and emulsifiers, especially for food applications. An estimated 1 to 2 million pounds of sorbitol go into making specialty polyethers for urethane foam production.

Methyl glucoside, obtained by the reaction of glucose or starch with methanol, has been produced and evaluated for a number of industrial applications. The most promising of these applications was for making polyethers for rigid polyurethane foam production. Although unfavorable economics earlier forced its removal from the market except for minor specialty uses, within the last few years a corn wet-miller began operating a facility for multi-million pound production of this polyol. Higher alkyl glucosides are made from methyl glucoside by a double alcohol interchange, first with n-butanol then with a  $C_8$  to  $C_{18}$  alcohol, or by reacting glucose with higher alcohols. These higher alkyl glucosides are sold commercially as nonionic detergents.

### **Polymers from Starch**

Research in the Plant Polymer Research Unit of the USDA/ARS Northern Regional Research Center has been directed mostly towards the potential of starch to replace in part, or in some instances in total, petroleum-derived synthetic polymers. Research areas include starch-plastic compositions, starch-synthetic polymer water absorbers, and starch matrices for encapsulation.

### **Starch in Plastics**

A large portion of the chemicals produced from petroleum is utilized to manufacture the nearly 55 billion pounds of synthetic polymers now used annually in the United States. Plastics, which now account for about 75% of the total synthetic polymer production, will double in usage volume during the next decade if raw materials are available. In recognition of this growth potential and the uncertainties in availability of sufficient petroleum feed stocks, interest has increased in the use of natural polymers as extenders for plastics or as total replacements for certain types of plastics. Not only is it the renewable aspect of raw materials such as starch that has

piqued the interest of industry, but also the potential of such natural polymers to impart biodegradability to fabricated materials.

Because of concern over buildup in the environment of discarded plastic goods due to their resistance to microorganisms, the plastics industry is giving attention to this area. If plastics can be made readily biodegradable, new markets for such materials would materialize and the growth for plastics would likely exceed even the most liberal estimates.

Starch has been evaluated as an inert filler in poly(vinyl chloride) (PVC) plastics, as a reactive filler in rigid urethane foams, and as a component in films containing poly(vinyl alcohol), poly(ethylene acrylic acid), polyethylene, and poly(ethylene-co-ethylene acrylic acid). Various techniques were investigated for incorporating large amounts of starch as a filler in PVC plastics. Starch-PVC films were prepared and their properties were measured in Weather-Ometer and outdoor exposure tests. By varying the composition, films were obtained that lasted from 40 to 900 hr. in the Weather-Ometer and from 30 to more than 120 days in the soil. All samples tested under standard conditions with common soil microorganisms showed mold growth, with the greatest amount of growth recorded for samples containing the highest amount of starch.

Griffin reported that starch can be incorporated into low-density polyethylene (LDPE) film to impart biodegradable properties. Based on this work, a company in England and one in Canada are now producing polyethylene bags that contain 7 to 10% starch and are reportedly biodegradable.

One area of application for biodegradable plastic film is as agricultural mulch. An estimated 125 million pounds of plastic mulch is used in the United States to improve the yield and quality of vegetable and fruit crops such as tomatoes, peppers, melons, and sweet corn. Mulch helps to control soil moisture and temperature, reduce nutrient leaching, prevent weed growth, and increase crop yields by 50 to 350% per acre. Polyethylene (PE) film, commonly used for mulch, does not degrade between growing seasons and must be removed from the field and buried or burned at an estimated cost of up to \$200 per acre. Considerable interest has been expressed in using a degradable mulch to obviate the need for removal and disposal. Unfortunately, starch is quite incompatible with PE. We have found that a commercially modified PE, poly(ethylene-co-acrylic acid) (EAA), blends well with gelatinized starch and the blend forms good films. Films made from this system require no plasticizer, yet they remain flexible even after exposure to water and drying. Although the mechanism is

not known, we envision that as internal bonding within the starch molecule is reduced during gelatinization and extrusion, new bonds are formed between the starch hydroxyls and the EAA carboxyl groups that retard retrogradation of the starch.

Several techniques have been explored for making the films. Initially, they were made by casting aqueous dispersions of starch and EAA. These films are promising for applications where up to 90% starch is needed for rapid biodegradation but where strength, flexibility, and water resistance are not critical. When lower levels of starch were used, good physical properties and water resistance were achieved; however, the cost could prohibit certain large-scale applications because casting is a relatively slow process and aqueous dispersions of EAA are more expensive than pelletized EAA.

A second method, which allowed the use of EAA pellets, involved premixing film formulations with excess water (50% of less solids concentration) at 90–100°C in heavy-duty Sigma- or Banbury-style mixers for 45 minutes. The resulting dough-like product was repeatedly extrusion-processed into strands until the moisture content of the extruded product was about 5 to 10%. The product was then blown into film by extruding it through a 0.5-inch blown film die. Small amounts of alkali were essential to obtaining quality film. Ammonium hydroxide is the preferred alkali for general purpose film because any excess readily escapes during processing of the films. When strong alkali is added, such as sodium hydroxide, the resulting films have semipermeable properties. This premixing method allows the addition of various formulating aids such as LDPE to lower the formulation cost or various polyols and sugars to increase the amounts of biodegradable composition. Films have been made by this method with up to 60% starch; however, the preferred maximum starch level is about 40–50%.

One major concern to potential manufacturers was the need to premix the starch and EAA in a heavy-duty mixer with large amounts of water before extrusion processing and blowing into film. Quality films have now been made without this premixing step and with much lower initial moisture, by incorporating urea into the system. The major function of the urea is to reduce the amount of water and time needed to gelatinize the starch. Using this technique, a 35-lb. pilot-plant run was successfully completed. A semidry composition of 45% EAA, 40% starch, and 15% urea plus about 17 parts per hundred of aqueous ammonium hydroxide was mixed in a ribbon blender and then extruded into small strands. The extruded product was fed through a commercial blown-film extruder by Rex Plas-

tics, Thomasville, NC. The extruder had a 2-inch diameter screw and a 4-inch die. The bubble had a lay-flat width of 12 inches.

In general, starch-EAA films had tensile strengths that remained constant at 2000–2300 psi, but their percentage elongation dropped from 130% to 20% as the starch level was increased from 20% to 50%. Substituting up to half of the EAA with LDPE caused some loss in both strength and percentage elongation, especially with aging; however, cost reduction may outweigh these slight property losses.

Incorporating 10–15% urea into a starch-EAA formulation, to eliminate the heavy-duty mixing step, lowered tensile strengths of films with 40% starch to about 1600 psi, but the percentage elongation increased slightly due to the plasticizing effect of urea. After soaking in water, which removed the urea, tensile strengths and percentage elongations were comparable to those made without urea, by the premixing method. Commercial development of this technology is underway following the granting of an exclusive license to our patent to a private company in 1987.

Another approach to starch-plastics compositions is to chemically bond the synthetic polymer to starch through graft polymerization. Basically, the procedure used for synthesizing starch graft polymer is to initiate a free radical on the starch backbone and then allow the radical to react with polymerizable vinyl or acrylic monomers. A number of free-radical initiating methods have been used to prepare graft copolymers, and these may be divided into two broad categories: initiation chemically and by irradiation. The choice depends in part on the particular monomer or combination of monomers to be polymerized. Both chemical and irradiation initiating systems have been employed to graft polymerize onto starch a wide variety of monomers, both alone and in selected combinations.

For plastic or elastomeric copolymer compositions that can be extruded or milled, monomers such as styrene, isoprene, acrylonitrile, and various alkyl acrylates and methacrylates were employed.

Starch graft-polystyrene, -poly(methyl methacrylate), -poly(methyl acrylate), and -poly(methyl acrylate-co-butyl acrylate) polymers have been prepared with approximately 50% add-on and evaluated for extrusion processing characteristics. A 20:80 (by weight) mixture of starch graft-polystyrene and commercial polystyrene produced an extrudate that was filled with particles of unfluxed graft copolymer after two passes through the extruder at 150°C. Addition of glycerol to the mixture as a plasticizer for starch did not greatly improve extrudate properties. However, when the graft copolymer was extruded at 175°C in the absence of additives, a con-

tinuous, well-formed extrudate was produced. Tensile strengths for specimens milled from the extrudate were in the range of 7,500–9,000 p.s.i.

Two starch graft-poly(methyl acrylate) products, one prepared from granular starch and the other from gelatinized starch, were extrusion processed under various conditions. The graft copolymer prepared from granular starch was extruded (three passes) through a  $1 \times 0.020$ -in. slit die at  $160^{\circ}\text{C}$  and a barrel temperature of  $150^{\circ}\text{C}$ . The extruded ribbon was smooth and translucent and exhibited good tensile strength (3,000 psi) and little die swell. Lower extrusion temperatures produced an extrudate which contained unfluxed polymer, and only a crumbly mass was obtained at  $125^{\circ}\text{C}$ .

The graft copolymer prepared from gelatinized starch was extruded (one pass) at  $125^{\circ}\text{C}$  with a die temperature of  $140^{\circ}\text{C}$  to give an extrudate which resembled that obtained from granular starch, but which was less brittle. When extruder and die temperatures were lowered to  $100^{\circ}\text{C}$ , a continuous plastic was still produced, although there was an appreciable amount of unfluxed polymer. Tensile strength of the higher temperature extrudate was on the order of 2,500 p.s.i., and die swell was minimal. Prolonged soaking of the extrudate in water at room temperature produced a white material that was soft and pliable and showed appreciable increases in both weight and thickness. The specimen surface, however, was not sticky, and the plastic remained continuous and showed no tendency to disintegrate. To estimate biodegradability, a portion of the extrudate was incubated for 5 days at  $25^{\circ}\text{C}$  with three different cultures in a nutrient solution, as suggested by ASTM D1924-70. *Aspergillus niger* and *Trichoderma viride* gave good growth and sporulation. *Penicillium funiculosum* produced little sporulation but gave good growth.

### Starch Graft Copolymers as Water Absorbers

A wide variety of other monomers have been graft polymerized onto granular and gelatinized starch, and several of the graft polymers show promise as thickeners for aqueous systems, flocculants, clarification aids for waste-waters, retention aids in papermaking, and many other uses. The polymer that has received the most attention and is now being produced by three U.S. companies is made by graft polymerizing acrylonitrile onto gelatinized starch and subjecting the resulting starch graft-polyacrylonitrile copolymer to alkaline saponification to convert the nitrile functionalities to a mixture of carboxamide and alkali metal carboxylate groups. Removing the water from this polymer provides a solid that ab-



sorbs many hundreds of times its weight of water but does not dissolve. Because of its ability to rapidly absorb such large amounts of water, it has been named Super Slurper. The U.S. Department of Agriculture has granted more than 75 nonexclusive licenses to parties interested in practicing the technology.

Aqueous dispersions of saponified gelatinized starch graft-polyacrylonitrile can be cast to yield films on drying. These films are brittle but can be plasticized to improve flexibility. Flexible films can be obtained on casting aqueous dispersions of the graft polymer containing an anionic or nonionic latex. The films will absorb several hundred times their weight of distilled water to give clear sheets of gel, which remain strong enough to maintain their integrity. Also, despite a thirtyfold increase in surface area upon imbibing water, the exact shape of the dry film is retained. Reducing the pH of the water to near 3 causes the gel sheet to retract to its original size, and raising the pH back to near 7 or higher causes the film to return to a highly swollen gel sheet.

Other forms of the absorbent polymer are obtained by alternate methods of drying. Alcohol precipitation yields a granular or powdery product, whereas drum drying affords flakes and freeze-drying give spongy mats. Selected enduse applications dictate the most desirable form of the product.

For application as an additive to absorbent soft goods such as disposable diapers, incontinent pads, bandages, hospital bedpads, and catamenials, interest has been expressed in the powder, film, and mat forms; the first two forms have been used commercially in disposable diapers, incontinent pads and hospital bed pads. The ability of the absorbent polymer to retain most of its absorbed fluid under pressure is a desirable property for such applications. Under a pressure of  $45 \times g$ , a Super Slurper product that had absorbed 648 times its weight of water still retained 409 times its weight. Cellulose fibers, on the other hand, initially absorbed 40 times their weight and retained only 2.1 times their weight under this pressure.

Partial hydration of the starch graft polymer provides a hydrogel especially effective in treating skin wounds of animals. The hydrogel absorbs large quantities of fluids secreted by the wounds, provides relief from pain, and prevents drying of subcutaneous tissue. Clinical trials with the hydrogel conducted with human patients suffering from decubitus ulcers or stasis ulcers gave excellent results. All skin ulcers responded favorably to the treatment, and the wounds either healed completely or developed a cleaner bed of granulation tissue. In every case the hydrogel dressing resulted in less eschar formation, fewer infections, and less odor than ulcers treated by

other methods. In early 1981 a medical supply company began marketing the product for use by humans.

Agricultural applications, such as for seed and root coating and as an additive to fast-draining soils to retain water, appear most promising for Super Slurper. Large-scale field trials with corn, soybean, and cotton seed coated with the polymer have shown increased germination and seedling emergence, and in most trials, increased yields. The dipping of bare-rooted, seedlings in hydrated polymer before transplanting overcomes transplant shock and greatly increases survival. For such applications, the powder or granular form is being used.

Grafting of acrylonitrile onto granular (rather than gelatinized) starch followed by saponification in an alcoholic medium also produces an absorbent product. The polymer produced by this route is being used in absorbent underpads.

### **Starch Encapsulation Matrix**

We have developed several technologies for encapsulating a broad range of chemical pesticides within a starch matrix to improve safety in handling and to reduce losses of the pesticide in the environment due to volatility, leaching, and decomposition by light. Initially we developed a procedure based on starch xanthate that consists of dispersing the active agent in an aqueous starch xanthate solution and subsequently crosslinking the starch xanthate either oxidatively, or with multivalent metal ions, or with difunctional reagents such as epichlorohydrin. Upon crosslinking, which is effected within a few seconds under ambient conditions, the entire mass becomes gel-like and, on continued mixing for an additional few seconds, becomes a particulate solid that can be dried to low moisture content with only minimal or no loss of the entrapped chemical. That only a single phase is produced on crosslinking with no supernatant is important in assuring essentially complete entrapment of both water-soluble and water-insoluble pesticidal chemicals.

Both solid and liquid pesticides have been encapsulated by this procedure. Where the pesticide is a liquid or finely divided solid, it is added as such to the aqueous solution. For pesticides provided as granular solids, they are first dissolved in an appropriate solvent and then added to the solution. We have made formulations containing up to 55% by weight of liquid pesticides and even higher amounts of solid compounds.

We have reported on other procedures for using starch as a matrix for encapsulation. In one, the pesticide is dispersed in alkali-treated starch

followed by coagulation with calcium chloride. This method overcomes the need for carbon disulfide, which is a flammable and toxic liquid required for making xanthates. In a second procedure, boric acid is used to coagulate a highly concentrated paste of alkali-treated starch that contains the dispersed pesticide. A gel is formed on addition of boric acid that is broken into small swollen particles, which after coating with dry starch or silica are suitable for drying.

Encapsulated herbicides have been prepared by these methods and have been evaluated in field trials. Because of the relative simplicity of the procedure that requires calcium chloride or boric acid, and because of the encouraging results from field studies with both types of encapsulated products, licenses to our patents have been granted to several companies and commercialization appears likely.

Because each of these encapsulation procedures employs chemical treatment of starch, little interest has been shown in the techniques to encapsulate flavors, nutrients, vitamins or medicaments for use in foods or feeds. Recently we discovered that such food or feed ingredients are readily and efficiently entrapped in a nonchemically modified starch matrix. By controlling the amylose to amylopectin ratio in the matrix through the use of different cornstarches or mixture of starches, matrices with different release properties are easily prepared. The procedure for encapsulation is simple, involving heating a high-solids, aqueous suspension of starch to effect gelatinization, adding the agent to be encapsulated and allowing retrogradation to occur during drying. The inherent property of amylose, and to a lesser extent amylopectin, to insolubilize through molecular association is effective in providing a crosslinked starch matrix that encapsulates added agents.

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